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Isobaric Vapor−Liquid Equilibria in the Systems Methyl 1,1-Dimethylethyl Ether + Methyl Ethanoate and Oxolane + Heptane

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Vapor−liquid equilibrium at 94 kPa has been determined for the binary systems methyl 1,1-dimethylethyl ether (MTBE) + methyl ethanoate and oxolane + heptane. The binary system MTBE + methyl ethanoate deviates moderately from ideal behavior, behaves almost like a regular solution, and presents an azeotrope that boils at 323.34 K and contains 62.1 mol % MTBE. The system oxolane + heptane shows moderate deviations from ideality and does not present an azeotrope. The activity coefficients and boiling points of both binary systems were well correlated with their composition by the Redlich−Kister, Wohl, Wilson, UNIQUAC, NRTL, and Wisniak−Tamir equations.

The 1990 Clean Air Act Amendments set stringent rules governing the quality and characteristics of gasoline used in the United States. These regulations have resulted in oxygenates like methyl 1,1-dimethyl ether (MTBE) and ethanol playing a significant role as gasoline octane improvers. Two of the compounds tested here are oxygenates that may be considered as additives for gasoline. MTBE is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability. Cyclic and aliphatic ethers are frequenly used in the chemical industry as solvents and intermediates. Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures. Deshpande and Oswal (1975) and Oswal and Deshpande (1988) have reported vapor−liquid equilibria, excess Gibbs function, and volume of mixing data for the system oxolane + heptane at temperatures from 298 to 313 K. No vapor−liquid equilibria data is available for the system MTBE + methyl ethanoate. The present work was undertaken to measure vapor−liquid equilibria (VLE) data for the title systems for which no isobaric data are available.

Experimental Section

Purity of Materials. Methyl 1,1-dimethylethyl ether (99.93 mass %), oxolane (99.9 mass %), and heptane (99.57 mass %) were purchased from Aldrich; methyl ethanoate (99.5 mass %) was purchased from Merck. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1.

Table 1. Mole Percent GLC Purities (mass %), Refractive Index n_D at the Na D Line, and Normal Boiling Points T of Pure Components

component (purity/mass %)	n_D (298.15 K)	T/K
methyl 1,1-dimethylethyl ether (99.93)	1.3661[a]	328.29[a]
	1.3663[b]	328.35[b]
methyl ethanoate (99.5)	1.3588[a]	330.05[a]
	1.3589[c]	330.09[c]
oxolane (99.9)	1.4050[a]	339.15[a]
	1.4049[d]	339.12[d]
heptane (99.57)	1.3851[a]	371.54[a]
	1.38513[e]	371.553[f]

[a] Measured. [b] TRC Tables, a-6040. [c] TRC Tables, a-5560. [d] TRC Tables, a-6170. [e] TRC Tables, f-1460. [f] TRC Tables, k-1460.

Apparatus and Procedure. An all-glass vapor−liquid-equilibrium apparatus model 602, manufactured by Fischer Labor-und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation method apparatus, about 100 mL of the solution is heated to its boiling point by a 250 W immersion heater (Cottrell pump). The vapor−liquid mixture flows through an extended contact line which guarantees an intense phase exchange and then enters a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned again to the immersion heater. Temperature control is achieved by a 5 mm diameter Pt-100 temperature sensor, with an accuracy of ±0.1 K. The total pressure of the system is controlled by a vacuum pump capable to work under vacuum up to 0.25 kPa. The pressure is measured by a Vac Probs with an accuracy of ±0.07 kPa. On the average the system reaches equilibrium conditions after 0.5−1 h operation. Samples, taken by syringing 0.7 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SE-30. Injector and detector temperatures for both binaries were 493.15 and 543.15 K respectively, and column temperatures were 323.15 K for the system methyl 1,1-dimethylethyl ether (MTBE) + methyl methanoate and 353.15 K for the system oxolane + heptane. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fit had a correlation coefficient R^2 better than 0.99. Concentration measurements were accurate to better than ±0.005 mole fraction.

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 94$ kPa are reported

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Table 2. Experimental Vapor–Liquid Equilibrium Data for Methyl 1,1-Dimethylethyl Ether (1) + Methyl Ethanoate (2) at 94 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/(cm^3 mol^{-1})	$-B_{22}$/(cm^3 mol^{-1})	$-B_{12}$/(cm^3 mol^{-1})	G^E/RT
327.75	0	0						0
326.95	0.046	0.074	1.5510	1.0044	776	586	586	0.024
326.55	0.072	0.111	1.5019	1.0055	779	588	588	0.034
325.85	0.127	0.184	1.4380	1.0057	783	591	591	0.051
325.45	0.184	0.249	1.3608	1.0047	785	594	594	0.061
324.55	0.299	0.365	1.2673	1.0200	790	598	598	0.085
323.95	0.398	0.452	1.2020	1.0468	793	601	601	0.101
323.65	0.520	0.543	1.1138	1.1087	795	603	603	0.106
323.45	0.566	0.583	1.1064	1.1263	796	604	604	0.109
323.35	0.615	0.622	1.0884	1.1576	797	605	605	0.108
323.35	0.630	0.619	1.0586	1.2119	797	605	605	0.107
323.45	0.684	0.667	1.0465	1.2371	796	604	604	0.098
323.55	0.732	0.705	1.0298	1.2891	796	604	604	0.089
323.65	0.771	0.740	1.0244	1.3189	795	603	603	0.082
323.95	0.812	0.778	1.0117	1.3596	793	601	601	0.067
324.15	0.829	0.801	1.0138	1.3293	792	600	600	0.060
324.35	0.888	0.860	1.0094	1.4152	791	599	599	0.047
324.95	0.943	0.926	1.0029	1.4416	788	596	596	0.024
325.35	0.973	0.961	0.9965	1.5385	785	594	594	0.008
325.75	1	1						0
$\gamma_i^{\infty\ a}$			1.59	1.63				

[a] Calculated according to Wisniak et al. (1996).

Table 3. Experimental Vapor–Liquid Equilibrium Data for Oxolane (3) + Heptane (4) at 94 kPa

T/K	x_3	y_3	γ_3	γ_4	$-B_{33}$/(cm^3 mol^{-1})	$-B_{44}$/(cm^3 mol^{-1})	$-B_{34}$/(cm^3 mol^{-1})	G^E/RT
368.55	0	0						0
365.55	0.036	0.125	1.5220	1.0031	793	1596	1146	0.018
359.55	0.123	0.330	1.3842	1.0085	827	1666	1196	0.047
356.95	0.168	0.411	1.3558	1.0114	842	1699	1218	0.061
356.35	0.181	0.432	1.3468	1.0090	846	1706	1223	0.061
352.35	0.275	0.544	1.2463	1.0391	870	1758	1260	0.088
351.85	0.292	0.565	1.2343	1.0319	873	1765	1264	0.084
349.85	0.345	0.614	1.2030	1.0552	886	1792	1283	0.099
348.75	0.364	0.634	1.2167	1.0673	893	1807	1294	0.113
347.95	0.395	0.652	1.1778	1.0978	898	1818	1302	0.121
344.55	0.525	0.745	1.1207	1.1477	921	1867	1336	0.125
342.75	0.618	0.796	1.0742	1.2128	934	1894	1355	0.118
340.75	0.714	0.847	1.0520	1.3016	948	1925	1376	0.112
339.55	0.788	0.884	1.0332	1.3859	957	1944	1389	0.095
338.45	0.859	0.918	1.0185	1.5303	965	1961	1402	0.076
338.25	0.880	0.934	1.0178	1.4581	967	1964	1404	0.061
338.15	0.884	0.934	1.0163	1.5127	968	1966	1405	0.062
337.75	0.907	0.945	1.0152	1.5906	971	1972	1409	0.057
337.45	0.931	0.959	1.0128	1.6264	973	1977	1413	0.045
337.15	0.949	0.969	1.0133	1.6867	975	1982	1416	0.039
336.70	1		1					0
$\gamma_i^{\infty\ a}$			1.68	1.73				

[a] Calculated according to Wisniak et al. (1996).

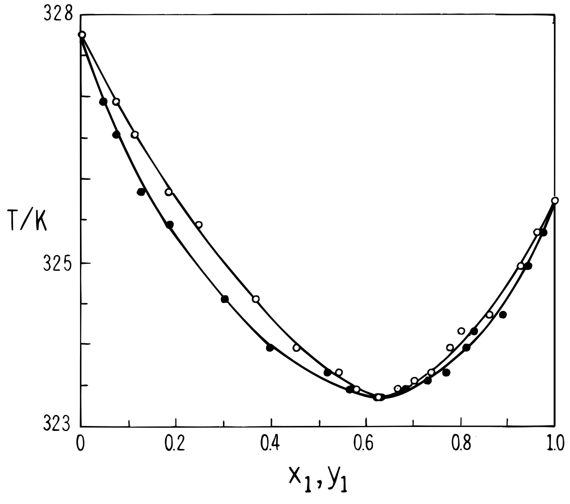

Figure 1. Boiling temperature diagram for the system methyl 1,1-dimethylethyl ether (1) + methyl ethanoate (2) at 94 kPa.

in Tables 2 and 3 and Figures 1 and 3, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \qquad (1)$$

where T and P are the boiling point and the total pressure, V_i^{L} is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (2)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 1 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The pure

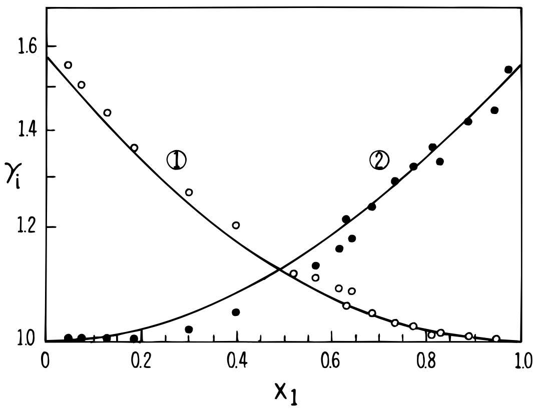

Figure 2. Activity coefficients for the system methyl 1,1-dimethylethyl ether (1) + methyl ethanoate (2) at 94 kPa: (○, ● experimental), (—) predicted by NRTL model.

Table 4. Antoine Coefficients, Eq 3

compound	A_i	B_i	C_i
methyl 1,1-dimethylethyl ether[a]	5.860 78	1032.988	59.876
methyl ethanoate[b]	6.186 213	1156.43	53.46
oxolane[c]	6.121 42	1203.11	46.795
heptane[d]	6.020 23	1263.909	56.718

[a] Reich (1996). [b] TRC Tables, a-5550. [c] TRC Tables, a-6170. [d] TRC Tables, k-1460.

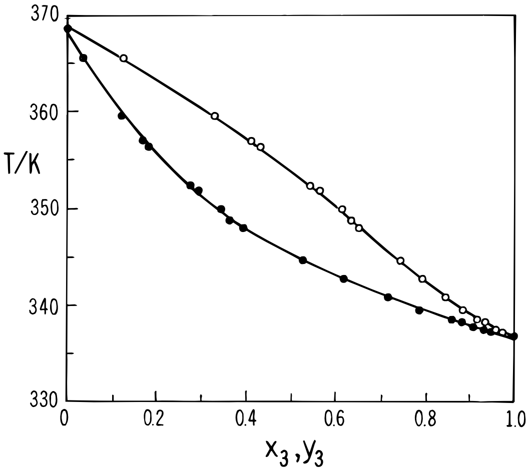

Figure 3. Boiling temperature diagram for the system oxolane (3) + heptane (4) at 94 kPa.

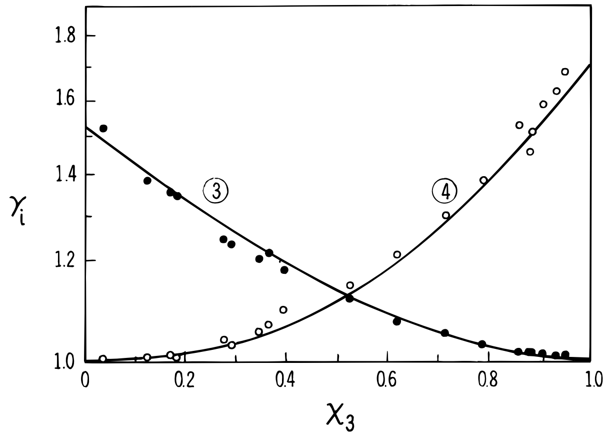

Figure 4. Activity coefficients for the system oxolane (3) + heptane (4) at 94 kPa: (○, ● experimental), (—) predicted by NRTL.

component vapor pressures P_i^0 were calculated according to the Antoine equation:

$$\log(P_i^0/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \tag{3}$$

where the Antoine constants A_i, B_i, and C_i are reported in Table 4. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of O'Connell and Prausnitz (1967) using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. Critical properties of MTBE were taken from a publication by Ambrose et al. (1974). The last two terms in eq 1, particularly the second one that expresses the correction due to the nonideal behavior of the vapor phase, contributed less than 3% to the activity coefficients of both binary systems; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables 2 and 3 and Figures 2 and 4 and are estimated accurate to within ±2%. The results reported in these tables indicate that the binary system MTBE + methyl ethanoate deviates moderately from ideal behavior and presents an azeotrope that boils at 323.34 K and contains 62.1 mol % MTBE. The system oxolane + heptane deviates moderately from ideality and does not present an azeotrope. Tables 2 and 3 contain also the

Table 5. Parameters and Deviations between Experimental and Calculated Values for G^E-Different Models

A. Redlich–Kister, Eq 4

system	B	C	D	max dev %[a]	avg dev %[b]	rmsd[c]
methyl 1,1-dimethylethyl ether (1) + methyl ethanoate (2)	0.1980			4.7	2.3	0.006
	0.1980	0.0028		4.4	2.3	0.006
oxolane (3) + heptane (4)	0.2082	0.0197	0.0233	5.1	2.4	0.006

B. Other Models[d]

model	system	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 2	0.4610	0.4457	1.046		0.0047
	3 + 4	0.4190	0.5619	0.7605		0.0107
Wilson	1 + 2	−39.23[f]	1378.2[f]			0.0046
	3 + 4	1414.1	197.46			0.0110
NRTL	1 + 2	403.42[f]	899.75[f]		0.543	0.0048
	3 + 4	1624.6	−95.334		0.314	0.0098
UNIQUAC	1 + 2	462.76[f]	14.833[f]			0.0060
	3 + 4	−114.95	14.130			0.0114

[a] Maximum deviation %. [b] Average deviation %. [c] Root mean square deviation. [d] All equations in ln γ_i form. [e] $\delta(y) = \sum|y_{\text{exptl}} - y_{\text{calcd}}|/N$ (N = number of data points). [f] J/mol.

Table 6. Coefficients in Correlation of Boiling Points, Eq 6, Average % Deviation, and Root Mean Square Deviations in Temperature, rmsd (*T*/K)

system	C_0	C_1	C_2	max dev %[a]	avg dev %[b]	rmsd[c]
methyl 1,1-dimethylethyl ether (1) + methyl ethanoate (2)	−12.569 32	−0.638 63	−4.549 40	0.4	0.14	0.02
oxolane (3) + heptane (4)	−29.069 15	16.082 23	−10.203 42	0.5	0.14	0.03

[a] Maximum deviation %. [b] Average deviation %. [c] Root mean square deviation.

activity coefficients at infinite dilution calculated by the method suggested by Wisniak et al. (1996).

The vapor−liquid equilibria data reported in Tables 2 and 3 were found to to be thermodynamically consistent by the *L*−*W* (point-to point and area) method of Wisniak (1993) and the point-to-point method of Van Ness et al. (1973) as modified by Fredenslund et al. (1977). For both binaries, the residuals of the Fredenslund test were randomly distributed, as measured by the Durbin−Watson statistic. The activity coefficients of both binary systems were correlated well with the Redlich−Kister, Wohl, Wilson, NRTL, and UNIQUAC equations (Walas, 1985). The following expression was used for the Redlich−Kister (1948) expansion

$$\log(\gamma_i/\gamma_j) = B(x_j - x_i) + C(6x_ix_j - 1) + D(x_j - x_i)(8x_ix_j - 1) \quad (4)$$

The values of the constants *B*, *C*, and *D* were determined by multilinear regression and appear in Table 5 together with the pertinent statistics. It is seen that the Redlich−Kister model gives a good representation of the data for both systems and that the behavior of the system MTBE + methyl ethanoate approximates that of a regular solution. The parameters of the Wohl, Wilson, NRTL, and UNIQUAC equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N,2}\left(\frac{\gamma_{i,\mathrm{exptl}} - \gamma_{i,\mathrm{calcd}}}{\gamma_{i,\mathrm{exptl}}}\right)^2 \quad (5)$$

and are reported in Table 5, together with the relative deviation of the vapor composition. Inspection of the results given in Table 5 shows that all four models fitted both binary systems very well, the best fit corresponding to the NRTL correlation. The capability of predicting the vapor phase composition has been used as the ranking factor.

The excess Gibbs function G^E of the two binary systems is presented in Tables 2 and 3 as the variation of the dimensionless function G^E/RT with concentration. The boiling points of the two binaries were correlated by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = x_iT_i^0 + x_jT_j^0 + x_ix_j\sum_{k=1}^{m}C_k(x_i - x_j)^k \quad (6)$$

In this equation T_i^0/K is the boiling point of the pure component at the operating pressure and *m* is the number of terms in the series expansion of $(x_1 - x_2)$. The various constants of eq 6 are reported in Table 6, which also contains information indicating the degree of goodness of the correlation.

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